

DECLARATION

I, Kazuhiro ISHII , a national of Japan,
c/o Asamura Patent Office of 331-340, New Otemachi
Building, 2-1, Otemachi-2-chome, Chiyoda-ku, Tokyo, Japan
do hereby solemnly and sincerely declare:-

- 1) THAT I am well acquainted with the Japanese language
and English language, and
- 2) THAT the attached is a full, true, accurate and
faithful translation into the English language made
by me of Japanese Patent Application No. 9-163717.

The undersigned declares further that all
statements made herein of his own knowledge are true and
that all statements made on information and belief are
believed to be true; and further that these statements
were made with the knowledge that willful false statements
and the like so made are punishable by fine or imprisonment,
or both, under section 1001, of Title 18 of the United
States Code and that such willful false statements may
jeopardize the validity of the application or any patent
issuing thereon.

Signed this 29th day of December , 2005



Kazuhiro ISHII

KANNO EXHIBIT 1004
Rossin v. Kanno
Contested Case 105,402

[Title of Document] Patent Application
[Reference Number] 1197016991
[Date of Submission] June 20, 1997
[Addressee] Commissioner
The Patent Office
[International Patent Classification] B01D 53/36
[Title of the Invention]
PROCESS FOR TREATING FLUORINE
COMPOUND-CONTAINING GAS
[Number of Claims for a Patent] 14

[Inventor]

[Address] c/o Hitachi Research Laboratory,
HITACHI, LTD., 1-1, Omikacho 7-chome,
Hitachi-shi, Ibaraki, Japan.

[Name] Shuichi KANNO

[Inventor]

[Address] c/o Hitachi Research Laboratory,
HITACHI, LTD., 1-1, Omikacho 7-chome,
Hitachi-shi, Ibaraki, Japan.

[Name] Shinzo IKEDA

[Inventor]

[Address] c/o Hitachi Research Laboratory,
HITACHI, LTD., 1-1, Omikacho 7-chome,
Hitachi-shi, Ibaraki, Japan.

[Name] Ken YASUDA

[Inventor]

[Address] c/o Hitachi Research Laboratory,
HITACHI, LTD., 1-1, Omikacho 7-chome,
Hitachi-shi, Ibaraki, Japan.

[Name] Hisao YAMASHITA

[Inventor]

[Address] c/o Hitachi Research Laboratory,
HITACHI, LTD., 1-1, Omikacho 7-chome,
Hitachi-shi, Ibaraki, Japan.

[Name] Shigeru AZUHATA

[Inventor]

[Address] c/o Hitachi Works, HITACHI, LTD., 1-1,
Saiwaicho 3-chome, Hitachi-shi,
Ibaraki, Japan.

[Name] Shin TAMADA

[Inventor]

[Address] c/o Hitachi Works, HITACHI, LTD., 1-1,
Saiwaicho 3-chome, Hitachi-shi,
Ibaraki, Japan.

[Name] Kazuyoshi IRIE

[Applicant]

[Applicant's ID Number] 0 0 0 0 0 5 1 0 8

[zip code] 101

[Address] 6, Kandasurugadai 4-chome, Chiyoda-ku,
Tokyo, Japan

[Name] HITACHI, LTD.

[Representative Director] Tsutomu KANAI

[Agent]

[Agent's ID Number] 1 0 0 0 6 8 5 0 4

[zip code] 100

[Address] c/o, HITACHI, LTD., 5-1, Marunouchi
1-chome, Chiyoda-ku, Tokyo, Japan

[Patent Attorney]

[Name] Masao OGAWA

[Telephone] 03-3212-1111

9-163717

[Indication on Fee]

[Prepayment Register Number] 0 1 3 0 8 8

[Amount of Payment] ¥21,000-

[List of Items Filed]

[Title of Article] Specification 1

[Title of Article] Drawings 1

[Title of Article] Abstract 1

[Number of General Power] 9003094

[Proof Required or not] yes

[Title of Document] Description

[Title of the Invention] PROCESS FOR TREATING FLUORINE COMPOUND-CONTAINING GAS

[Claims]

5 [Claim 1]

A process for decomposition treating a fluorine-containing compound, which comprises contacting a gas stream containing a compound containing fluorine as a halogen with a catalyst containing Al in the presence of an effective amount of water vapor at a temperature of about 200 to 800°C to convert the fluorine in the gas stream to hydrogen fluoride.

10 [Claim 2]

A process for decomposition treating a fluorine-containing compound, which comprises contacting a gas stream containing a compound containing fluorine as a halogen with a catalyst containing Al and at least one member selected from the group consisting of Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, Si and P in the presence of an effective amount of water vapor at a temperature of about 200 to 800°C to convert the fluorine in the gas stream to hydrogen fluoride.

15 [Claim 3]

The process according to Claim 2, wherein the catalyst further contains S.

20 [Claim 4]

The process according to Claim 2, wherein the catalyst contains constituting components in the form of an oxide of each component singly or as a composite oxide of Al and other component.

5 [Claim 5]

A process for decomposition treating a fluorine-containing compound, which comprises contacting a gas stream containing a halogen compound having fluorine as a halogen and carbon such as CF_4 , CHF_3 , C_2F_6 , 10 C_3F_8 , C_4F_8 , and C_5F_8 with a catalyst containing Al in the presence of an effective amount of water vapor at a temperature of about 200 to 800°C to decompose the halogen compound to at least one of CO and CO_2 , and HF.

[Claim 6]

15 A process for decomposition treating a fluorine-containing compound, which comprises contacting a gas stream containing a halogen compound having fluorine and S such as SF_6 with a catalyst containing Al in the presence of an effective amount of water vapor at 20 a temperature of about 200 to 800°C to decompose the halogen compound to at least one of SO_2 and SO_3 , and HF.

[Claim 7]

A process for decomposition treating a fluorine-containing compound, which comprises contacting 25 a gas stream containing a halogen compound having fluorine and N such as NF_3 with a catalyst containing Al in the presence of an effective amount of water vapor at a temperature of about 200 to 800°C to decompose the..

halogen compound to at least one of NO and NO₂, and HF.

[Claim 8]

A process for decomposition treating a fluorine-containing compound, which comprises contacting 5 a gas stream containing a halogen compound having fluorine as a halogen with a catalyst containing Al in the presence of an effective amount of water vapor at a temperature of about 200 to 800°C to convert the fluorine in the gas stream to hydrogen fluoride, 10 followed by neutralization of the decomposed products of the halogen compound with an alkali.

[Claim 9]

A catalyst for decomposition treating a fluorine-containing compound, characterized by using for 15 decomposition of a halogen compound containing fluorine as a halogen in contact with a water vapor, and containing Al.

[Claim 10]

A catalyst for decomposition treating a 20 fluorine-containing compound, characterized by using for decomposition of a halogen compound containing fluorine as a halogen in contact with a water vapor, and containing Al and at least one member selected from Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, Si and Pt, the atomic ratio 25 of Al:M (wherein M is Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, or Si) being 50 to 99% by mole of Al and 50 to 1% by mole of M, and containing Pt in the range of 0.1 to 2% by weight based on 100% by weight of Al₂O₃.

[Claim 11]

The catalyst according to Claim 10, which further contains 0.1 to 20% by weight of S.

[Claim 12]

5 The catalyst according to Claim 10, wherein each component is present in the form of an oxide of each component singly or a composite oxide of Al and other component.

[Claim 13]

10 An apparatus for decomposition treatment of a fluorine-containing compound, which comprises a reactor packed with a catalyst containing Al; a gas addition device for adding either of nitrogen, oxygen or air to the halogen compound to be introduced into the reactor 15 to give a gas stream; a heating device for heating either one of the gas stream or the reactor packed with the catalyst at a temperature of about 200 to 800°C; a steam addition device for adding an effective amount of water vapor for decomposing the halogen compound to the 20 gas stream; and an exhaust gas washing tank for washing decomposition products of the halogen compound produced by contact of the catalyst with the gas stream in the reactor with an alkali solution followed by neutralization.

25 [Claim 14]

The apparatus according to Claim 13, which further comprises an adsorption device for adsorbing the decomposition products not neutralized by the alkali

washing in a later stage of the exhaust gas washing tank.

[Detailed Description of the Invention]

[0001]

5 [Technical Field Pertinent to the Invention]

The present invention relates to a process for decomposition treatment of compounds having fluorine as a halogen such as CF_4 and the like effectively at a low temperature.

10 [0002]

[Prior Art]

Halogen compound gases containing only fluorine as a halogen such as CF_4 and the like are used in a large amount as semiconductor etchers, 15 semiconductor cleaners and the like. However, it was found that when these substances are discharged into the atmosphere, global warming took place.

[0003]

Gases such as CF_4 , etc. have fluorine (F) in a 20 large amount as a molecular constituting element. The fluorine is the highest in electronegativity among all the elements and forms chemically very stable substances. Particularly, CF_4 and the like are strong in intramolecular force and substances poor in reactivity. 25 From these properties, a high temperature is necessary for decomposition such as combustion and a large amount of energy is consumed therefor. Further, the

decomposition reaction at high temperatures produces gases such as hydrogen fluoride, etc. which are large in corrosion ate of apparatus materials. It is thus in the current situations that no appropriate processes for 5 such decomposition treatment are not available yet.

As the decomposition treatment processes, there is proposing a combustion technology at a high temperature. But, according to this process, since a flammable gas such as propane or the like is used, a 10 large amount of CO₂ and NO_x which is a harmful substance are produced by combustion. Further, since the flammable gas such as propane is used, there is a danger of explosion. Further, due to combustion near 1000°C, a corrosive gas is produced by the decomposition of the 15 halogen compound and damages the furnace wall, resulting in enhancing the maintenance frequency and enlarging the operation cost. Therefore, a technology which can decompose at lower temperatures without producing harmful substances is necessary.

20 [0004]

As to the catalysts for decomposing halogen compounds, there have been filed various patent applications. But, there is no report as to the decomposition of halogen compounds containing only 25 fluorine as a halogen which gas is aimed at in the present invention. According to JP-A-3-66388, there is a description that no decomposition function is shown for CF₄ which contains only fluorine as a halogen

according to said invention. In addition, as disclosed in Chem. Lett. (1989) pp. 1901-1904, Okazaki et al have tried to hydrolyze CFC-14(CF_4) using Fe_2O_3 /active carbon, but no decomposition took place.

5 [0005]

[Problem to be solved by the Invention]

An object of the present invention is to provide a process for efficient decomposition treatment of halogen compounds containing only fluorine as a halogen such as CF_4 , etc. at low temperatures, a catalyst for decomposition having a high decomposition rate and a long catalyst life, and an apparatus for such a decomposition treatment.

[0006]

15 [Means for Solving Problem]

The present inventors have studied decomposition treatment processes wherein halogen compounds containing only fluorine as a halogen such as CF_4 can be decomposed at low temperatures with high efficiency and an apparatus is hardly corroded with corrosive gases in the decomposed gases, and as a result, the present invention is attained.

[0007]

That is, it was found that when a gas stream containing a halogen compound having only fluorine as a halogen is contacted with a catalyst containing Al in the presence of an effective amount of water vapor at about 200 to 800°C, the halogen compound is decomposed

to convert the fluorine in the gas stream into hydrogen fluoride.

[0008]

The halogen compound containing only fluorine 5 as a halogen such as CF_4 which is the gas of object is strong in the intramolecular force due to properties of fluorine having high electronegativity, and a substance poor in reactivity, so that it is hardly decomposed by the reaction with oxygen. That is, by adding H_2O , it is 10 possible to obtain a high decomposition rate for the first time.

[0009]

The halogen compound which is the object of the present invention is a halogen compound containing 15 only fluorine as a halogen. Constituting components include fluorine, carbon, oxygen, sulfur, nitrogen, etc. Examples of the compound include CF_4 , CHF_3 , CH_2F_2 , CH_3F , C_2F_6 , C_2HF_5 , $\text{C}_2\text{H}_2\text{F}_4$, $\text{C}_2\text{H}_3\text{F}_3$, $\text{C}_2\text{H}_4\text{F}_2$, $\text{C}_2\text{H}_5\text{F}$, C_3F_8 , $\text{CH}_3\text{OCF}_2\text{CF}_3$, C_4F_8 , C_5F_8 , SF_6 , NF_3 , etc.

20 [0010]

As the catalyst of the present invention, there is a catalyst containing Al. The Al in the catalyst is present as an oxide or as a composite oxide with other metal(s). Or, it is possible to use a 25 catalyst containing at least one component selected from Zn, Ni, Ti, Fe, Sn, Pt, Co, Zr, Ce and Si other than Al. Further, when S is added to these catalysts, decomposition activity of the catalysts can be enhanced.

[0011]

Necessary things for catalyst performances are to have a high decomposition rate and a long catalyst lifetime. As a result of detailed studies of catalysts 5 showing these performances, it was found that even Al_2O_3 single body can have a high decomposition performance depending on raw materials. As a raw material, there can be used boehmite, and the like. Powders therefrom are dried, and fired at a suitable temperature to give 10 an Al_2O_3 catalyst which shows a high decomposition activity.

[0012]

In order to obtain a high decomposition rate, there can be used a catalyst containing at least one 15 component selected from Zn, Ni, Ti, Fe, Sn, Pt, Co, Zr, Ce, and Si together with Al. In this catalyst, Al is present in the form of Al_2O_3 , or a composite oxide of the added metal component(s). Zn, Ni, Ti, Fe, Sn, Pt, Co, Zr, Ce, and Si are present in the form of oxides or 20 composite oxides with Al. In these catalysts, the atomic ratio of Al : M (M = Zn, Ni, Ti, Fe, Sn, Co, Zr, Ce, Si) is preferably 50 to 99% by mole of Al and 50 to 1% by mole of M. Further, Pt is preferably contained in an amount of 0.1 to 2% by weight based on 100% by weight 25 of Al_2O_3 . M can be one component or more than one components, but in the case of more than one component, the total amount of metal components is preferably in the range of 50 to 1% by mole. When the adding

component is too much, the decomposition activity of Al₂O₃ is suppressed.

[0013]

Further, in order to obtain a long catalyst lifetime, it is effective to suppress crystallization of Al₂O₃ in the catalyst, and also to form a composite oxide of Al and an added metal component such as NiAl₂O₄, ZnAl₂O₄ and the like. As a method for improving the catalyst performance, there is a method of adding S into the catalyst. As a method of adding S, there can be employed a method of using a sulfate, or using sulfuric acid, or the like at the time of preparing the catalyst. The S in the catalyst is present in the form of SO₄ ion, etc. to function for strengthening the acid properties of the catalyst. The amount of S is preferably from 0.1 to 20% by weight.

[0014]

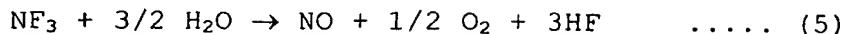
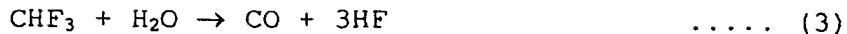
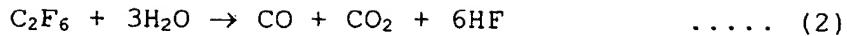
According to the decomposition treatment process of the present invention, it is possible to add oxygen into the gas stream containing the halogen compound such as CF₄. It is also possible to use the oxidation reaction of CO and the like in the decomposed gas.

[0015]

Typical reactions among decomposition reactions of the halogen compounds are as follows.

[0016]





5 Reactions according to reaction equations (2) and (3) can produce CO. The present catalysts also have an ability to oxidize CO, and thus CO can be further oxidized to CO₂ in the presence of oxygen.

[0017]

10 The amount of water vapor to be added is to be adjusted so that hydrogen molecules are present in an amount at least equal to the number of F among the halogen compound to be treated. By this, the fluorine in the compound can be converted to hydrogen fluoride, 15 which is easy for aftertreatment.

[0018]

The reaction temperature used in the present invention is preferably about 200 to 800°C. Particularly as to the halogen compounds constituted by 20 at least carbon, fluorine and hydrogen, about 500 to 800°C is preferable. When higher temperatures than the above-mentioned is used, higher decomposition rates may be obtained, but the catalysts are degraded rapidly. Further, the corrosion rate of the apparatus materials 25 becomes large suddenly. On the other hand, the temperatures lower than the lower limit, the decomposition rate is low.

[0019]

In contacting of the gas stream containing the halogen compound having only fluorine as a halogen with the catalyst, the content of the halogen compound in 5 the gas stream is preferably 0.1 to 10% by volume, particularly preferably 0.1 to 3% by volume, and the space velocity is preferably 100 to 10,000 h^{-1} , particularly preferably 100 to 3,000 h^{-1} . Space velocity (math) h^{-1} is defined by reaction gas flow rate 10 (ml/h)/catalyst volume (ml).

[0020]

As the step for removing after neutralization of a part of hydrogen fluoride, carbon dioxide, a part of oxides of sulfur such as SO_2 , SO_3 , etc., and a part of 15 nitrogen oxides such as NO , NO_2 , etc., a step of spraying an alkali solution for washing is preferable because of high efficiency and hardly bringing about clogging of pipes due to deposition of crystals. It is also possible to use a process wherein produced gases by 20 decomposition are bubbled in an alkali solution, or a process wherein washing is conducted by using a packed column. Further, it is possible to use an alkaline solid. As the alkali, there can be used conventional alkali reagents such as an aqueous solution, a slurry or 25 the like of potassium hydroxide or sodium hydroxide.

[0021]

As the Al raw material for preparing the catalyst of the present invention, there can be used γ -

alumina, a mixture of γ -alumina and δ -alumina, and the like. It is also a preferable method to use boehmite or the like particularly as the Al raw material, followed by firing to form the oxide.

5 [0022]

As the raw materials for various metal components for preparing the catalysts of the present invention, there can be used nitrates, sulfates, ammonium salts, chlorides and the like. As the raw 10 material for Ni, there can be used nickel nitrate, and nickel sulfate. These hydrates can also be used. As the raw material for Ti, there can be used titanium sulfate, titania sol, and the like.

[0023]

15 The catalyst of the present invention can be prepared by any of ordinary procedures for preparing catalysts, such as a precipitation method, an impregnation method, a kneading method, etc.

[0024]

20 The catalyst of the present invention can be used as such or upon molding into a granular form, a honeycomb form, etc. by a desired molding procedure such as extrusion molding, tabletting, tumbling granulation, etc., or as a coating on ceramic or metallic honeycombs 25 or plates.

[0025]

The reactor used for practicing the treating process of the present invention includes an ordinary

fixed bed, moving bed or fluidized bed reactor. Since corrosive gases such as HF and the like are produced as decomposition product gases, the reactor should be constructed by materials hardly damaged by these

5 corrosive gases.

[0026]

The treating apparatus used for practicing the treating process of the present invention comprises the reactor mentioned above, a means for adjusting the 10 concentration of the halogen compound in the gas stream, for example, a means for supplying nitrogen, or air or oxygen to the gas stream, a means for heating at least one of the gas stream and the catalyst in order to contact them at a temperature of 200 to 800°C, a means 15 for adding water vapor to the gas stream in an amount sufficient to decompose the halogen compound, and an exhaust gas washing tank wherein decomposition products of halogen compound produced by contacting the gas stream with the catalyst packed in the reactor are 20 washed with an alkali aqueous solution for neutralizing a part of carbon dioxide, a part of sulfur oxides such as SO₂, SO₃, and the like, a part of nitrogen oxides such as NO, NO₂, and the like, and hydrogen fluoride in the decomposition products. It is further preferable to 25 provide a means for adsorption with an adsorber to adsorb carbon monoxide, sulfur oxides, and nitrogen oxides in the decomposition products not neutralized by alkali washing in the later stage of the exhaust gas.

washing tank.

[0027]

It is possible to apply the treating process for halogen compound-containing gases of the present invention to already constructed semiconductor factories. Since a semiconductor factory generally has an exhaust gas treating apparatus, it is possible to use such an apparatus while placing only the catalyst of the present invention in the exhaust gas line for halogen compounds such as CF_4 , and adding water vapor followed by heating to conduct decomposition treatment of halogen compounds.

[0028]

The whole or part of the apparatus of the present invention can be mounted on a truck or the like and moved to a place wherein wasted halogen compounds are stored in a bomb to directly treat the halogen compounds by drawing out them for treatment. Further, it is possible to mount a circulatory pump for circulating the washing solution in the exhaust gas washing tank, and an exhaust gas adsorption tank for adsorbing carbon monoxide, etc. in the exhaust gas at the same time. In addition, it is possible to mount an electric generator and the like.

25 [0029]

The decomposition treatment process for halogen compounds of the present invention can decompose the halogen compounds at lower temperatures than other

treating processes, so that the operation cost can be reduced.

[0030]

When halogen compound-containing gases are 5 treated, there arises a problem of corrosion of apparatus materials by acid components produced by decomposition such as HF and the like. According to the present invention, since the temperature used is low, the corrosion rate is small. Thus, the maintenance 10 frequency of the apparatus can be reduced.

[0031]

The decomposition treatment process of halogen compounds of the present invention comprises a catalytic reaction step for decomposing the halogen compounds and 15 an exhaust gas washing step for removing neutralized acid components in the decomposition product gases, so that the apparatus can be minimized.

[0032]

The halogen compounds are reacted with water 20 vapor, so that safety as the decomposition treatment process is high and there is no dangers such as explosion in the case of using flammable gases.

[0033]

[Mode for Carrying out the Invention]

25 Hereinafter, the present invention is explained in detail referring to Examples, but not limited thereto.

[0034]

Fig. 1 shows an example of a decomposition treatment process of halogen compounds when used in a semiconductor etching step.

[0035]

5 In the etching step, a halogen compound 1 such as CF₄ is supplied to an etching furnace under reduced pressure, excited by plasma for 20 minutes to react with a semiconductor. Then, the chamber is replaced by N₂ 2 to dilute the concentration of the halogen compound to 10 several percents, followed by discharge from the etching furnace at about 10 l./min.

[0036]

To the discharged gas, air 3 is added to dilute the halogen compound such as CF₄. At that time, 15 nitrogen can be added for dilution. Further, the dilution can be done by adding nitrogen and oxygen. To this diluted gas, water vapor 4 is added to give a reaction gas 5, which is sent to a decomposition step. The concentration of halogen compound in the reaction 20 gas is about 0.5 to 1%. In the decomposition step, the reaction gas 5 is contacted with Al₂O₃ series catalyst at 700°C under the condition of space velocity of 1000 per hour [space velocity (h⁻¹) = reaction gas flow rate (ml/h) / catalyst volume (ml)]. In this case, the 25 reaction gas can be heated, and the catalyst can be heated by an electric furnace and the like. The decomposed gas 6 is led to the exhaust gas washing step. In the exhaust gas washing step, the decomposition gas 6

is sprayed with an alkali aqueous solution to remove acid components in the decomposition gas and the resulting exhaust gas 7 is discharged to system outside. The decomposition rate of the halogen compound such as 5 CF₄ is obtained from the analysis data of the reaction gas 5 and the exhaust 7 using FID (flame ionization detector) gas chromatograph and TCD (thermal conductivity detector) gas chromatograph, and material balance at the inlet and the outlet.

10 [0037]

[Example 1]

In this Example, activities of various halogen compound decomposition catalysts are examined.

[0038]

15 A C₂F₆ gas having a purity of 99% or more was diluted with air, and the diluted gas was further admixed with steam. Steam was prepared by feeding pure water to a reactor tube from the top at a flow rate of about 0.2 ml/min. by a microtube pump to gasify the pure 20 water. The reaction gas had a C₂F₆ concentration of about 0.5%, and was brought into contact with a catalyst heated to a predetermined temperature by external heating of the reactor tube in an electric oven at a space velocity of 2,000 h⁻¹.

25 [0039]

The reactor tube was an Inconel reactor tube having an inner diameter of 32 mm and had a catalyst bed fixed at the center of the reactor tube. An Inconel

thermowell for a thermocouple, 3 mm in diameter, was inserted into the catalyst bed. Decomposition product gas from the catalyst bed was bubbled through an aqueous calcium fluoride solution and discharged to the system 5 outside. The decomposition rate of C_2F_6 was obtained by the following equation using FID gas chromatograph and TCD gas chromatograph:

[0040]

[Expression 1]

$$\text{Decomposition rate} = 1 - \frac{\text{Halogen compound at outlet}}{\text{Halogen compound fed}} \times 100 \text{ (%)}$$

10 [0041]

The following catalysts were prepared for the test under the foregoing conditions:

[0042]

Catalyst 1:

15 Boehmite powders of commercially available were dried at 120°C for one hour. 200 g of the resulting dried powders were fired at 300°C for 0.5 hour and at 700°C for 2 hours. The resulting powers were placed in a mold and compression molded under a pressure of 500 20 kgf/cm². The molded article was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The catalyst after completion consists of Al_2O_3 .

[0043]

Catalyst 2:

Boehmite powders of commercially available were dried at 120°C for one hour. To 200 g of the resulting dried powders, an aqueous solution dissolving 5 85.38 g of zinc nitrate hexahydrate was added and kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm 10 and tested. The resulting grain composition for catalyst was in an atomic ratio of Al : Zn = 91 : 9 (mole %).

[0044]

Catalyst 3:

15 Boehmite powders of commercially available were dried at 120°C for one hour. 200 g of the resulting dried powders were admixed with an aqueous solution of 50.99 g of nickel sulfate hexahydrate and the mixture was kneaded. After kneading, the kneaded mixture was 20 dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm. The resulting grain composition for catalyst was in an atomic ratio of Al : Ni = 91 : 9 (mole %).

25 [0045]

Catalyst 4:

Boehmite powders of commercially available were dried at 120°C for one hour. 300 g of the resulting

dried powders were admixed with an aqueous solution of 125.04 g of nickel nitrate hexahydrate and the mixture was kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 5 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm. The resulting grain composition for catalyst was in an atomic ratio of Al : Ni = 91 : 9 (mole %).

[0046]

10 Catalyst 5:

Boehmite powders of commercially available were dried at 120°C for one hour. 300 g of the resulting dried powders were kneaded with 354.4 g of an aqueous 30% titanium sulfate solution while adding about 300 g 15 of pure water thereto. After kneading, the kneaded mixture was dried at 250° - 300°C for about 5 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The resulting grain 20 composition for catalyst was in an atomic ratio of Al : Ti = 91 : 9 (mole %).

[0047]

Catalyst 6:

Boehmite powders of commercially available 25 were dried at 120°C for one hour. 200 g of the resulting dried powders were admixed with an aqueous solution of 115.95 g of iron nitrate nonahydrate and the mixture was kneaded. After kneading, the kneaded mixture was dried

at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm, and tested. The resulting grain composition was in 5 an atomic ratio of Al : Fe = 91 : 9 (mole %).

[0048]

Catalyst 7:

Boehmite powders of commercially available were dried at 120°C for one hour. 200 g of the resulting 10 dried powders were admixed with an aqueous solution of 95.43 g of tin chloride hydrate and the mixture was kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and 15 sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The resulting grain composition for catalyst was in an atomic ratio of Al : Sn = 91 : 9 (mole %).

[0049]

20 Catalyst 8:

Boehmite powders of commercially available were dried at 120°C for one hour. 200 g of the resulting dried powders were admixed with an aqueous solution prepared by diluting 22.2 g of a dinitrodiamino Pt(II) 25 nitric acid solution (Pt concentration: 4.5 wt.%) with 200 ml of pure water, and the mixture was kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2

hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The resulting grain composition for catalyst contained 0.68% by weight of Pt based on 100% 5 by weight of Al_2O_3 .

[0050]

Catalyst 9:

Boehmite powders of commercially available 10 were dried at 120°C for one hour. 300 g of the resulting dried powders were admixed with an aqueous solution of 125.87 g of cobalt nitrate hexahydrate, and the mixture was kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and 15 sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The resulting grain composition was in an atomic ratio of Al : Co = 91 : 9 (mole %)

[0051]

Catalyst 10:

20 Boehmite powders of commercially available were dried at 120°C for one hour. 200 g of the resulting dried powders were admixed with an aqueous solution of 76.70 g of zirconyl nitrate dihydrate, and the mixture was kneaded. After kneading, the kneaded mixture was 25 dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The resulting grain composition for

catalyst was in an atomic ratio of Al : Zr = 91 : 9 (mole %).

[0052]

Catalyst 11:

5 Boehmite powders of commercially available were dried at 120°C for one hour. 200 g of the resulting dried powders were admixed with an aqueous solution of 124.62 g of cerium nitrate hexahydrate, and the mixture was kneaded. After kneading, the kneaded mixture was 10 dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The resulting grain composition for catalyst was in an atomic ratio of Al : Ce = 91 : 9

15 (mole %).

[0053]

Catalyst 12:

Boehmite powders of commercially available were dried at 120°C for one hour. 300 g of the resulting 20 dried powders were admixed with an aqueous solution of 129.19 g of 20 wt.% silica sol, and the mixture was kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and 25 sieved to obtain grains having grain sizes of 0.5 - 1 mm and tested. The resulting grain composition for catalyst was in an atomic ratio of Al : Si = 91 : 9 (mole %).

[0054]

Test results of the foregoing Catalysts 1 - 12 at a reaction temperature of 700°C are shown in Fig. 2. Reasons for Catalyst 3 having higher activity than 5 Catalyst 4 seems to be the effect of S.

[0055]

[Example 2]

In this Example, the composition of Al and Ni in Catalyst 4 in Example 1 was changed to give 10 catalysts, activities of which are examined and shown.

[0056]

Catalyst 4-1:

Boehmite powders of commercially available 15 were dried at 120°C for one hour. 200 g of the resulting dried powder were admixed with an aqueous solution of 8.52 g of nickel nitrate hexahydrate, and the mixture was kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and 20 sieved to obtain grains having grain sizes of 0.5 - 1 mm. The resulting grain composition for catalyst was in an atomic ratio of Al : Ni = 99 : 1 (mole %).

[0057]

Catalyst 4-2:

25 Boehmite powders of commercially available were dried at 120°C for one hour. 300 g of the resulting powders were admixed with an aqueous solution of 66.59 g of nickel nitrate hexahydrate, and the mixture was

kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm. The resulting grain composition for catalyst was in an atomic ratio of Al : Ni = 95 : 5 (mole %).

[0058]

Catalyst 4-3:

Boehmite powders of commercially available 10 were dried at 120°C for one hour. 200 g of the resulting dried powders were admixed with an aqueous solution of 210.82 g of nickel nitrate hexahydrate, and the mixture was kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 15 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm. The resulting grain composition for catalyst was in an atomic ratio of Al : Ni = 80 : 20 (mole %).

[0059]

20 Catalyst 4-4:

Boehmite powders of commercially available 25 were dried at 120°C for one hour. 200 g of the resulting dried powders were admixed with an aqueous solution of 361.16 g of nickel nitrate hexahydrate, and the mixture was kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1.

mm. The resulting grain composition for catalyst was in an atomic ratio of Al : Ni = 70 : 30 (mole %).

[0060]

Catalyst 4-5:

5 Boehmite powders of commercially available were dried at 120°C for one hour. 200 g of the resulting dried powders were admixed with 562.1 g of nickel nitrate hexahydrate, and the mixture was kneaded while adding water thereto. After kneading, the kneaded 10 mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm. The resulting grain composition for catalyst was in an atomic ratio of Al : Ni = 60 : 40 15 (mole %).

[0061]

Activities of the above-mentioned Catalyst 4 and 4-1 to 4-5 were examined in the same manner as in Example 1 except for changing the concentration of C_2F_6 20 to 2% and the supplying amount of pure water to about 0.4 ml/min. Decomposition rates after 6 hours from the beginning of the test are shown in Fig. 3.

[0062]

[Example 3]

25 In this Example, the composition of Al and Zn in Catalyst 2 in Example 1 was changed to prepare various catalyst and activities thereof were examined.

[0063]

Catalyst 2-1:

Boehmite powders of commercially available
were dried at 120°C for one hour. 200 g of the resulting
dried powders were admixed with an aqueous solution of
5 215.68 g of zinc nitrate hexahydrate and the mixture was
kneaded. After kneading, the kneaded mixture was dried
at 250° - 300°C for about 2 hours and then fired at 700°C
for 2 hours. The fired product was pulverized and
sieved to obtain grains having grain sizes of 0.5 - 1
10 mm. The resulting grain composition for catalyst was in
an atomic ratio of Al : Zn = 80 : 20 (mole %).

[0064]

Catalyst 2-2:

Boehmite powders of commercially available
15 were dried at 120°C for one hour. 200 g of the resulting
dried powders were admixed with 369.48 g of zinc nitrate
hexahydrate and the mixture was kneaded. After
kneading, the kneaded mixture was dried at 250° - 300°C
for about 2 hours and fired at 700°C for 2 hours. The
20 fired product was pulverized and sieved to obtain grains
having grain sizes of 0.5 - 1 mm. The resulting grain
composition for catalyst was in an atomic ratio of Al :
Zn = 70 : 30 (mole %).

[0065]

25 Catalyst 2-3:

Boehmite powders of commercially available
were dried at 120°C for one hour. 126.65 g of the
resulting dried powders were admixed with an aqueous

solution of 96.39 g of zinc nitrate hexahydrate, and the mixture was kneaded. After kneading, the kneaded mixture was dried at 250° - 300°C for about 2 hours and then fired at 700°C for 2 hours. The fired product was 5 pulverized and sieved to obtain grains having grain sizes of 0.5 - 1 mm. The resulting grain composition for catalyst was in an atomic ratio of Al : Zn = 85 : 15 (mole %).

[0066]

10 Activities of the above-mentioned Catalysts 2, 2-1 to 2-3 were examined in the same manner as in Example 1 except for changing the concentration of C_2F_6 to 2% and the supplying amount of pure water to about 0.4 ml/min. The decomposition rates after 6 hours from 15 the beginning of the test are shown in Fig. 4.

[0067]

[Example 4]

This Example shows the results of decomposition of CF_4 and CHF_3 . The test conditions are 20 the same as those of Example 1 except for changing the space velocity to 1000 per hour, and using nitrogen in place of air for diluting the halogen compounds. The catalyst used was Catalyst 4-3 in Example 2. Test results for each reaction temperature are shown in Fig.

25 5.

[0068]

[Example 5]

This Example shows the results of examination

of influences of steam upon C_2F_6 decomposition. The test conditions are the same as those in Example 1 except for changing the space velocity to $1,000\text{ h}^{-1}$. The catalyst 4 in Example 1 was used at a reaction temperature of 700° .

5 The test was carried out by supplying steam for 2 hours from the start of test, then interrupting supply of steam. After 5 hours, steam was supplied again. Test results are shown in Fig. 6.

[0069]

10 [Example 6]

This Example shows the results of decomposition of SF_6 . The test conditions are the same as those of Example 1 except for using a SF_6 gas having a purity of 99% or more, changing the space velocity was 15 to $1,000\text{ h}^{-1}$ and using nitrogen in place of air for diluting SF_6 . As the catalyst, Catalyst 4-3 in Example 2 was used. The reaction temperature was 700°C . The amount of SF_6 in the reaction gas at the inlet of the reactor tube and the amount of SF_6 in the decomposition 20 gas after passing the alkali absorption tank were determined by TCD gas chromatograph and the decomposition rate was calculated by the following equation. It was found that the decomposition rate was 99% or more.

25 [0070]

[Expression 2]

$$\text{Decomposition rate} = 1 - \frac{\text{Amount of F}_6 \text{ at the outlet}}{\text{Amount of fed SF}_6} \times 100 \text{ (%)}$$

[0071]

[Example 7]

This Example shows the results of decomposition of NF_3 . The test conditions are the same as those of Example 6 except for using a NF_3 gas having a purity of 99% or more. Reaction temperature was 700°C. The amount of NF_3 in the reaction gas at the inlet of the reactor tube and the amount of NF_3 in the decomposition gas after passing the alkali absorption tank were determined by TCD gas chromatograph and the decomposition rate was calculated according to the following equation. It was found that the decomposition rate was 99% or more.

[0072]

[15] [Expression 3]

$$\text{Decomposition rate} = \frac{\text{Amount of NF}_3 \text{ at the outlet}}{\text{Amount of fed NF}_3} \times 100 \text{ (%)}$$

[0073]

[Effects of the Invention]

According to the present invention, halogen compounds having only fluorine as a halogen such as CF_4 , C_2F_6 , etc. can be subjected to decomposition treatment

with high efficiency.

[Brief Description of the Drawings]

[Fig. 1]

5 A drawing showing a treatment process of Example 1 of the present invention.

[Fig. 2]

A drawing showing performances of each catalyst.

10 [Fig. 3]

A drawing showing performances of each catalyst.

[Fig. 4]

A drawing showing performances of each catalyst.

[Fig. 5]

A drawing showing performances of each catalyst.

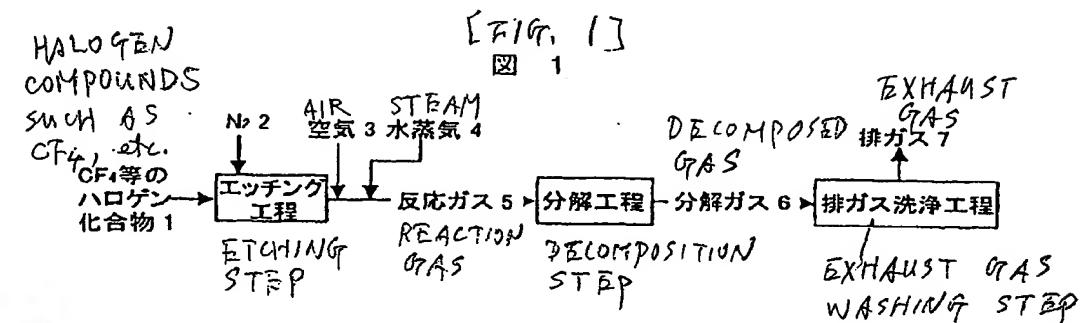
[Fig. 6]

20 A drawing showing performances of each catalyst.

[Description of Reference Numerals]

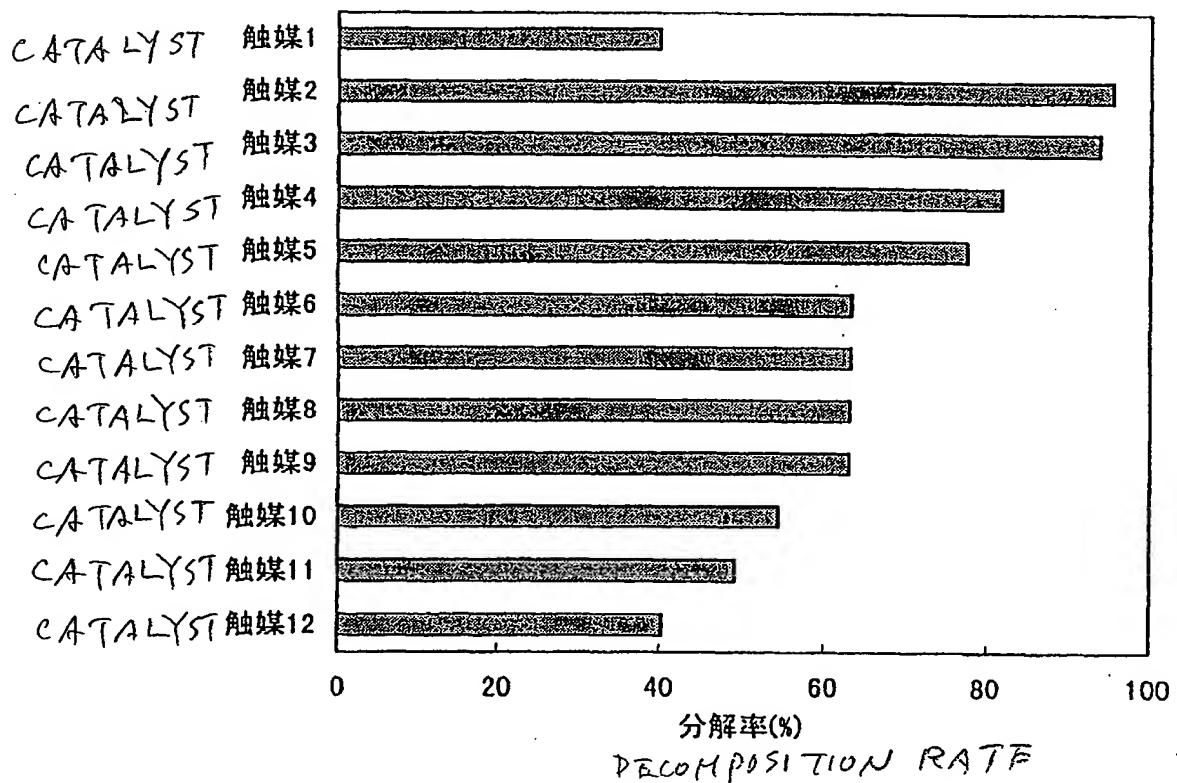
1 ... halogen compound such as CF_4 , 2 ... N_2 ,
3 ... air, 4 ... steam, 5 ... reaction gas,
25 6 ... decomposed gas, 7 ... exhaust gas

【書類名】 図面 [kind of Document] Drawings
 【図 1】



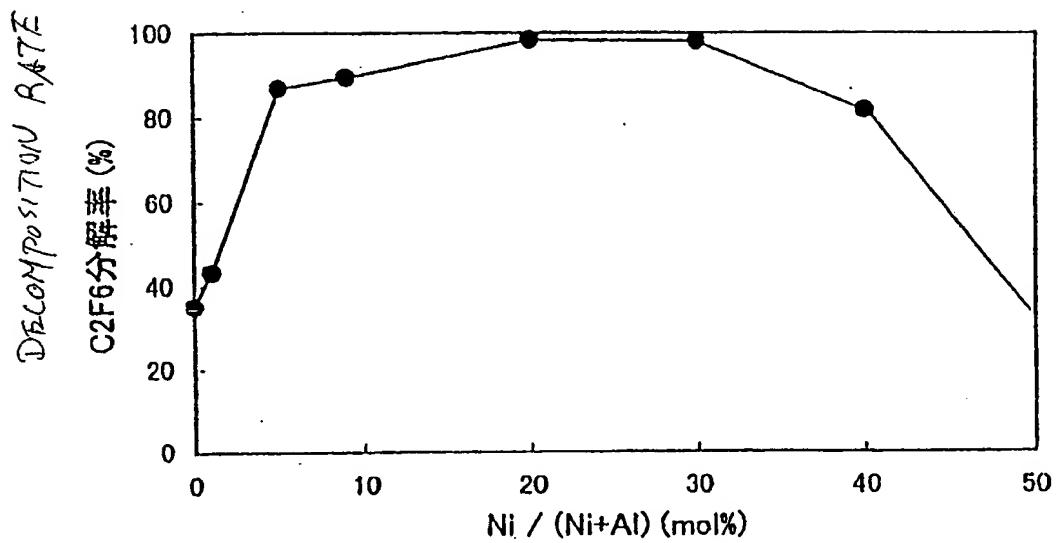
【図 2】

図 2 FIG. 2



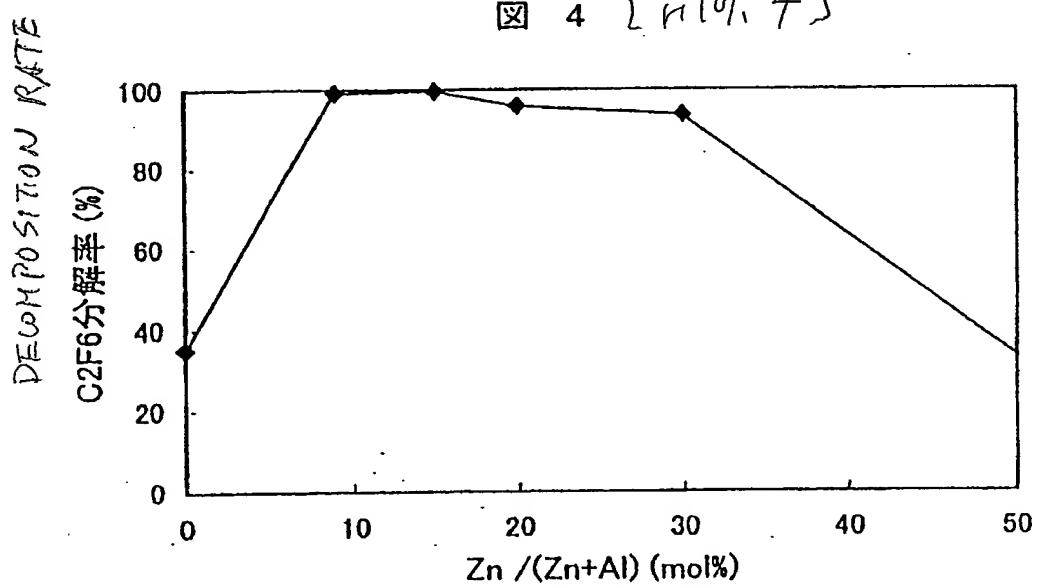
【図 3】

[FIG. 3]
図 3



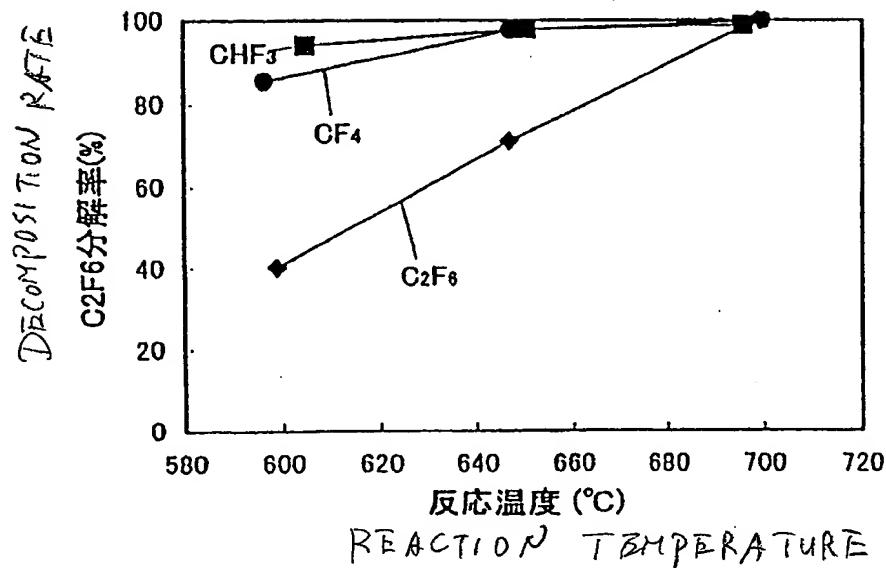
【図 4】

図 4 [FIG. 4]



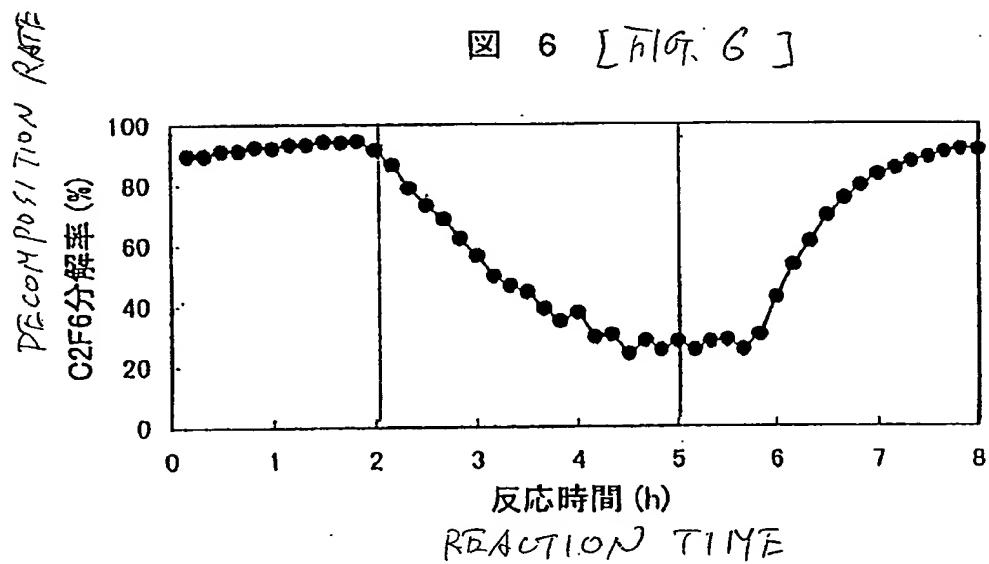
【図 5】

図 5 [FIG. 5]



【図 6】

図 6 [FIG. 6]



[Title of Document] Abstract

[Abstract]

[Problem] To provide decomposition treatment of halogen compounds containing only fluorine as a halogen such as CF_4 . C_2F_6 , etc. with high efficiency.

[Solution]

A gas stream containing halogen compounds containing only fluorine as a halogen is contacted with a catalyst containing Al in the presence of an effective amount of stream at about $200^\circ - 800^\circ\text{C}$, to convert the fluorine in the gas stream to hydrogen fluoride.

[Advantages]

Halogen compounds containing only fluorine as a halogen can be subjected to decomposition treatment with high efficiency.

[Selected Drawing] Fig. 2